UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
GROUND WATER AND ECOSYSTEMS RESTORATION DIVISION
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OFFICE OF
RESEARCH AND DEVELOPMENT

May 3, 2013

MEMORANDUM

SUBJECT: Review of the *Bench-Scale Treatability Study And Proposed Pilot-Scale Final Design Report* (Eli Lilly & Company) for the Evonik Degussa Corporation Tippecanoe Laboratories Site, Tippecanoe County, Indiana (13RC05-001)

FROM: David S. Burden, Ph.D., Director
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TO: Donald Heller, RPM
U.S. EPA Region V

Introduction

Technical support was requested to review the *Bench-Scale Treatability Study And Proposed Pilot-Scale Final Design Report* (Report). The request concerns remediation efforts relating to the Eli Lilly & Company site (i.e., the Evonik Degussa Corporation's Tippecanoe Laboratories location (Site)) located in the city of Lafayette in Tippecanoe County, Indiana.

The review was conducted under my direction, by Dr. Daniel Pope of CB&I, a contractor to EPA's Ground Water and Ecosystem Restoration Division. If you have any questions, please contact me at your convenience.

The Site includes a plateau surrounded by valley areas on the north, south, and west including the Wabash River and the Big Wea Creek drainage areas. For the plateau, a sand and gravel interval (Unit I) reaches from the surface to about 65 feet. A clayey till unit (with some fine silty sand discontinuous lenses) of up to 80 feet (Unit II) is below Unit I. Contaminants of concern (COCs) include benzene, chlorobenzene (CB), p-chlorobenzotrifluoride (pCBT), tetrahydrofuran (THF), and n,n-diethylaniline (n,n-DEA). The proposed treatment train includes in-situ chemical oxidation (ISCO) in source areas, followed by enhanced bioremediation, and finally, monitored natural attenuation (MNA) in the source and plume areas.

The Report details the results of a bench-scale ISCO test. The Report indicates that: "a Bench-Scale Treatability Study was completed to confirm that the primary COCs can be effectively treated by the chosen chemical oxidants." Six bench-scale microcosm tests were conducted using soils and ground water from three Site source areas – the Main Plant Source Area, the T1831 Floodplain Source Area, and the T1855 Source Area.

ISCO reagents used in the bench-scale test include solutions of 10% sodium persulfate (Klozur™), 10% Fe-EDTA, 10% calcium peroxide, 10% RegenOx™, and 10% Chemically Oxygenated GAC (COGAC®). Combinations of these reagents, as described in *Table 2 – Test Amendments* of the Report, were used for the bench-scale test. The combinations of these ISCO reagents are designated as SPFE-AT1, SPFE-AT2, COGAC-AT3, REGOX-AT4, and CPFE-AT5 in the bench-scale tests; the control, with no ISCO reagents, is designated as STAN-AT6.

General Comments

In general, the results of the bench-scale test indicate that ISCO could contribute to a significant reduction of concentrations of many of the Site COCs, assuming management of the full-scale ISCO operation was appropriate. It seems worthwhile to proceed with the pilot-scale ISCO tests.

However, some characteristics of the way the bench-scale study was conducted mean that there is considerable uncertainty connected with interpretation and application of the results.

Replicates

There were no replicate microcosms; that is, it appears that there was only one microcosm (i.e., one 1-liter "test vessel", as they are denoted in the Report) for each treatment condition (soil sample source X ISCO treatment). Therefore, there is no way to measure variability within each treatment condition, no way to estimate confidence limits for the results, and so no way to properly determine whether the differences between treatments are due to treatment effects or just variability (e.g., in the materials, procedures, or ISCO reagents). For example, data from replicates probably would help with the problem mentioned on p30 of the Report: "Soil heterogeneity with high soil concentrations is also the likely cause of the greater variability in initial concentrations between jars within this test set [T1831 shallow] compared to the other test sets."

Mass Balance, and Losses of COCs Not Due to ISCO Treatment

The Report mentions numerous times that there were losses of COCs during (or perhaps before) the bench-scale test not due to ISCO treatment. Due to these (explained as volatilization) losses, the control vessels ("standard" sample vessels) were used to calculate losses due to the ISCO treatments:

> "For the purposes of the bench-scale study, it was assumed that the desorption or volatilization measured in the standard sample vessel also occurred in each of the other test vessels; therefore, a corrected concentration or mass reduction was calculated from the actual observed reduction." (p32)

However, it is not clear just when these losses may have occurred, whether in transport of the water/soil samples to the bench-scale testing facility, or during mixing of the soils at the facility ("For each bench-scale test set, the multiple soil containers were homogenized into one batch from which a total of 1,800 grams of soil were collected and separated into six 1-liter, small mouth jars to be used as the test vessels" p29), or during the bench-scale testing itself. Also, there may have been mislabeling or mishandling of samples which could have led to COC losses (or apparent losses); the Report noted that there were errors in conducting the bench-scale tests due to a mixup with samples (p29 of the Report), though these were claimed to have been corrected.

However, what is clear that somehow through the sample collection process to the final results, possibly significant portions of the COCs appear to have been lost (i.e., not due to treatment by ISCO), as mentioned several times in the Report (p29, 30, 31, 32).

In order to better understand the bench-scale test results, a total mass balance, with the starting masses calculated from the initial analyses on ground-water and soil samples (*Table 1: Water Split Sample Results*, and *Table 2: Soil Split Sample Results*), and the ending masses calculated from *Table 4: Post-Treatment Water Results*, and *Table 5: Post-Treatment Soil Results*) should be calculated and provided in a table (i.e., in addition to the calculated data in *Table 6: Summary of Concentration and Mass Reductions*, which are estimates of the mass reduction due solely to treatment effects), so that the mass of the COCs lost to volatilization or other factors not due to the ISCO treatment, and the mass of COCs lost that can be attributed to treatment effects (i.e., ISCO) can be compared.

Note that because the T1855 soil was a composite of several soil samples, and it appears that there was no analysis done on that composite sample (e.g., as in the Soil Split samples (*Table 2: Soil Split Sample Results*)), the T1855 microcosms cannot have a mass balance done in this manner.

The water samples results listed in *Table 3: Pre-Treatment Water Results* could be used along with *Table 4: Post-Treatment Water Results* to calculate mass balances during the bench-scale study itself (i.e., not including sample acquisition, handling, transport, preparation, and addition to the test vessels), but due to the large number of COCs with different properties, the necessity of the assumption of complete COC equilibrium between soil and water, etc.), there would be considerable uncertainty connected with interpretation of the results.

If significant portions of COCs have been lost to volatilization (or other unknown process; i.e., not the ISCO treatment) during sample preparation or during the bench-scale test itself, the results of the test could be of questionable utility. That is (for example), if significant portions of COCs were lost before the test, then the tests could be considered as not being run on samples

representative of actual field conditions. Or, the contaminant mass loss due to the treatment might be minor compared to the contaminant mass loss required in the field, if a large fraction of the contaminant mass had been lost from the bench-scale samples due to volatilization. Again, if significant portions of COCs were lost (not due to ISCO treatment effects) during sample preparation or during the test, the techniques and methodology used could be questioned, leading to a lack of confidence in the results.

Calculations

Table 6: Summary of Concentration and Mass Reductions provides the results of calculations related to reduction of contaminant concentration and mass in the various test vessels used in the bench-scale tests including the "percent reduction in adsorbed-phase concentrations [i.e., the soil COC concentrations], normalized with the soil standard concentration".

Apparently these results are based on comparing the ISCO test data results (i.e., the ending soil COC concentration values in the SPFE-AT1, SPFE-AT2, COGAC-AT3, REGOX-AT4, and CPFE-AT5 test vessels) with the control results (the ending soil COC concentrations in the STAN-AT6 test vessels); these COC ending concentration values are found in *Table 5: Post Treatment Soil Results*.

However, it is not clear how the "qualified" data (e.g., qualified with a "J" or a "<") in Table 5 were handled, because a simple percent reduction calculation with the qualified data did not give the same results as found in Table 6, in a spot check of some of the data. When the qualified concentration data were used for the calculation, the percent reduction results were somewhat lower than those in Table 6; for nonqualified data, the numbers matched those in Table 6.

Specific Comments

Page 22 of the Report indicates:

> "Groundwater samples collected from existing monitor well T2011, new monitor wells T2015 and T2016, and new injection wells SW-IW-1, SW-IW-2, and SW-IW-3 were composited with soil samples collected from T2015, T2016, SW-IW-1, SW-IW-2, and SW-IW-3, and included in one bench-scale test set for the T1855 Source Area."

There is no starting contaminant concentration value for these composite samples (soil or water), apparently, and no information on how the samples were composited (i.e., proportions of each sample in the composite sample).

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> "For each bench-scale test set, the multiple soil containers were homogenized into one batch from which a total of 1,800 grams of soil were collected and separated into six 1-liter, small mouth jars to be used as the test vessels."

This step appears to a likely place for significant loss of volatiles.

It also appears that there were no replicates – no duplicate treatments to determine variability associated with the tests.

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> "Each of the test vessels was agitated for 30 seconds, placed in refrigeration (maintained at 5°C), and allowed to equilibrate for several days. This was done to allow the adsorbed-phase and dissolved-phase COCs to equilibrate in each media and replicate subsurface conditions as closely as possible while still providing enough groundwater for the required laboratory analysis…
>
> At this point in the bench-scale test, 280 ml of water was extracted from each vessel with a hypodermic needle…. the samples were shipped to Heritage for analysis of VOCs… These samples were collected to provide a baseline for each sample set prior to the addition of the test amendments. The above methodology was developed by Remington over the last several years, during which they have conducted over one hundred such tests and have become familiar with potential variables inherent in the methodology that can lead to spurious results."

It would be useful for Remington to provide a short discussion of the "potential variables inherent in the methodology that can lead to spurious results".

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> "The results of the split groundwater and soil samples that were directly submitted to Heritage from the field for analysis are presented in Tables 1 and 2 within Appendix B. These results were used for comparison to the pre-treatment water sample results and the post-treatment soil sample results."

It should be specified where in the Report these comparisons were made.

Table 6: Summary of Concentration and Mass Reductions

For some of the COCs, the calculated reduction values are listed as "NA"; it is not clear why this is the case.

cc: Charles Maurice, Region 5